PRESSURE-VELOCITY EQUILIBRIUM HYDRODYNAMIC MODELS*

Dedicated to Professor James Glimm on the occasion of his 75th birthday

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Abstract This article describes mathematical models for phase separated mixtures of materials that are in pressure and velocity equilibrium but not necessarily temperature equilibrium. General conditions for constitutive models for such mixtures that exhibit a single mixture sound speed are discussed and specific examples are described.

Key words Euler equations; multiple phase mixtures; non-equilibrium temperature mixtures

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1 Introduction

A major area of computational fluid dynamics is the treatment of material mixtures. In this article we will discuss some of the mathematical consequences of multiple material mixture models, in particular models that are "close" to single material formulations in the sense that the model is described by a single mixture pressure, velocity, and sound speed. Such models are useful due to their well-posedness, and their ability to be fitted into existing hydrocode implementations. The most popular of these is the pressure-temperature-velocity equilibrium model, which assumes that the material components in a computational cell are phase separated and in pressure and temperature equilibrium with a common velocity. Traditionally this model is referred to as a pressure-temperature (P-T) equilibrium model, with velocity equilibrium understood. However for time scales dominated by shock wave interactions, the P-T equilibrium assumption tends to be overly diffusive, and mixture models that relax this assumption are needed. In this article will discuss the mathematical structure of models obtained by relaxing the requirement of temperature equilibrium, while maintaining phase separation and pressure and temperature equilibrium.

Computational treatments for multiple material flows can be roughly broken up into three categories, interface treatments that attempt to resolve the material separations by explicitly tracking the boundaries between separate components (such as explicit geometric front tracking [5, 9, 10, 11, 12, 13, 14, 17] or level set methods [2, 22, 23, 34]), mixed cell treatments for the interactions between materials [4], and hybrid treatments such as the volume of fluid method [20, 26, 38, 39] that use both mixed cell models together with reconstructions of the interfaces between materials. Ideally all three methods can be combined into one computational system to provide both the high fidelity interface representation provided by tracking with the robustness of the mixed cell treatments.

The choice of a mixed cell model is extremely problem dependent, and must be based on the length and time scales appropriate for a given application. For example the assumption of pressure-temperature-velocity equilibrium for a mixture might be based on the following assumptions:

1) The microstructure of the mixture consists of volumetrically distinct components.

2) Material components are separated by interfaces/contact discontinuities across which pressure and the interfacial normal component of velocity are continuous.

3) Surface tension between components in the microstructure is negligible (no capillarity due to the microstructure).

4) Shear across the microstructure interface is negligible (common velocity). The assumption basically asserts that the microstructure consists of material components that are "well mixed", either as separate blobs of material, or convoluted interfaces between the components.

5) The application time scales are sufficiently long that the components have time to come into thermal equilibrium due to un-modeled processes such as thermal conduction (common temperature).

Our main interest in this article is to investigate the mathematical structure of models that relax this last condition, so that the microscopically separated components are not required to be in temperature equilibrium. More complicated models that allow multiple pressures and/or velocities in the microstructure are also of great interest but are beyond the scope of the models considered here. One of the aims for this set of models are to produce equations that are "close", to the P-T equilibrium model and thus are suitable to be retro-fitting into existing P-T equilibrium code implementations.

The group of Saurel et.al. has published an extensive set of articles describing two component mixtures. These works include Godunov schemes for pressure-relaxation models similar to the Baer-Nunziato [3] multiphase detonation model [27, 28], discretized forms of this model [1], extensions to turbulent flows [28, 30], applications to heterogeneous explosives [6], incorporation of capillarity effects in the model [24], evaporative front treatments [16], shock jump relations [8, 31], relaxation-projection schemes [25, 29], metastable fluid models [32], and efficient solution schemes for these type models [33]. In all of these models, the general limit of the flow in the case of infinite relaxation is a single pressure model with possibly multiple component temperatures. In many cases the relaxation parameters are treated as numerical "knobs", and often (but not always) the solution of interest is the limit under infinite relaxation rates.

As we will see, such single pressure models have an infinite set of possible closure relations, each corresponding to possibly different flow physics of the mixture. We will show that four

basic models in common usage can be included in this class, pressure-temperature equilibrium, volume-temperature equilibrium, entropy advection (thermal isolation), and volume fraction advection (uniform strain or uniform compression). Additional models can be built out of this set by assuming the flow has the nature of a "mixture of mixtures", for example components are themselves mixtures of materials in pressure-temperature or volume-temperature equilibrium. We will also examine what consequences the flow model assumption has on the shock wave structure of the material. This is non-trivial since generally the full model is not in conservative form and consequently the Rankine-Hugoniot equation for shocks is under-determined. As an example we will discuss a possible application of such mixture models to radiation hydrodynamics. Another major goal of this work will be to treat the multiple material mixture models for general equations of state, including the possibilty of phases that undergo physical phase changes.

2   Thermodynamic Preliminaries

The notation we use is that of Menikoff and Plohr [18]. The introduction to book of Israel [37] by A. S. Wightman also is very helpful in the thermodynamic discussion. These articles contain a number of useful thermodynamic identities that we will use freely. We assume that each material in the mixture is governed by a separate thermodynamically consistent equation of state, specifically we assume the existence of a C^1, piecewise C^2, convex specific internal energy $e = e(V, S)$ for each species (in subsequent sections we will distinguish the separate specific internal energy functions by a subscript for each material, here we suppress the subscript for clarity of notion) as a function of specific volume $V = \frac{1}{\rho}$ (ρ is the mass density) and specific entropy S in the interior of a convex domain $(V, S) \in \Omega_{V,S} \subseteq \{(V, S) \,|\, V > 0, S \geq 0\}$, and that $e(V, S)$ is lower semi-continuous at the boundary $\partial\Omega_{V,S}$. Since the specific internal energy is convex, lower semi-continuity of e is equivalent to the statement that at any point on $\partial\Omega_{V,S}$, e is either continuous or blows up as it approaches the boundary (see Niculescu and Persson [21]). The temperature and pressure of the material is given by the first law of thermodynamics relation:

$$\mathrm{d}e = T\mathrm{d}S - P\mathrm{d}V. \tag{1}$$

Thus $T = \frac{\partial e}{\partial S}\big|_V$ and $P = -\frac{\partial e}{\partial V}\big|_S$. In addition, we assume that for fixed specific volume, the specific internal energy is a monotone increasing function of specific entropy, thus $T \geq 0$ and we can invert the relation $e = e(V, S)$ to obtain a C^1 concave entropy function $S(V, e)$ with convex domain $\Omega_{V,e}$. Note that the Hessians of $e = e(V, S)$ and $S = S(V, e)$ are related by the formula:

$$\begin{bmatrix} \dfrac{\partial^2 S}{\partial V^2}\bigg|_e & \dfrac{\partial^2 S}{\partial V \partial e} \\[2mm] \dfrac{\partial^2 S}{\partial V \partial e} & \dfrac{\partial^2 S}{\partial e^2}\bigg|_V \end{bmatrix} = -\frac{1}{T^3} \begin{bmatrix} T & P \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \dfrac{\partial^2 e}{\partial V^2}\bigg|_S & \dfrac{\partial^2 e}{\partial V \partial S} \\[2mm] \dfrac{\partial^2 e}{\partial V \partial S} & \dfrac{\partial^2 e_k}{\partial S^2}\bigg|_V \end{bmatrix} \begin{bmatrix} T & 0 \\ P & 1 \end{bmatrix}. \tag{2}$$

Since strict convexity is equivalent to the statement that the Hessian matrix is positive definite, it is clear that S is strictly concave at $(V, e\,(V, S))$ if and only if e is strictly convex at $(V, S(V, e))$.

The equivalence of the concavity of $S(V, e)$ and the convexity of $e(V, S)$ follows immediately

from monotonicity of the entropy/energy relation for fixed specific volume, since for $0 < \alpha < 1$,

$$e\left((1-\alpha)V_0 + \alpha V_0, (1-\alpha)S_0 + \alpha S_1\right) \leq (1-\alpha)e(V_0, S_0) + \alpha e(V_1, S_1),$$

if and only if

$$(1-\alpha)S(V_0, e_0) + \alpha S(V_1, e_1) \leq S\left((1-\alpha)V_0 + \alpha V_0, (1-\alpha)e_0 + \alpha e_1\right),$$

where $e_0 = e(V_0, S_0)$ and $e_1 = e(V_1, S_1)$.

The sound speed c, Grüneisen exponent Γ, and the specific heat at constant volume C_V are defined by

$$
\begin{aligned}
\rho^2 c^2 &= -\left.\frac{\partial P}{\partial V}\right|_S = \left.\frac{\partial^2 e}{\partial V^2}\right|_S, \\
-\Gamma\frac{T}{V} &= \left.\frac{\partial T}{\partial V}\right|_S = \left.\frac{\partial^2 e}{\partial V \partial S}\right|, \\
\frac{T}{C_V} &= \left.\frac{\partial T}{\partial S}\right|_V = \left.\frac{\partial^2 e}{\partial S^2}\right|_V.
\end{aligned}
\tag{3}
$$

In regions where $e(V, S)$ is twice differentiable, convexity is equivalent to the conditions:

$$
\begin{aligned}
\rho^2 c^2 &> 0, \\
\rho^2 T^2\left(\frac{c^2}{C_V T} - \Gamma^2\right) &> 0, \\
\frac{T}{C_V} &> 0.
\end{aligned}
\tag{4}
$$

The relation between pressure and temperature, and specific volume and specific entropy can be inverted via the Legendre transformation:

$$G(P, T) = \inf_{(V,S)\in\Omega_{V,S}} \{e(V, S) + PV - TS\}. \tag{5}$$

The quantity $G(P, T)$ is the Gibb's free energy with convex domain

$$\Omega_{P,T} = \{(P, T) | G(P, T) > -\infty\}.$$

Similarly one can invert the relation between entropy and temperature to derive the Helmholtz free energy:

$$F(V, T) = \inf_{S|(V,S)\in\Omega_{V,S}} \{e(V, S) - TS\}, \tag{6}$$

with domain

$$\Omega_{V,T} = \{(V, T) | F(V, T) > -\infty\}.$$

For a convex C^1 function $e(V, S)$, it can be shown (see [21] again) that $G(P, T)$ is strictly concave, upper semi-continuous (convex/concave functions are always continuous in the interior of their domains), piecewise C^1, and that at locations where $G(P, T)$ is differentiable, it satisfies the relation:

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T. \tag{7}$$

Furthermore the slope of a curve along which the partials of $G(P,T)$ jump satisfy the Clausius-Clapeyron equation:

$$\left.\frac{\mathrm{d}P}{\mathrm{d}T}\right|_{\mathrm{coex}} = \frac{\Delta S}{\Delta V}. \tag{8}$$

Pressures and temperatures where the Gibb's free energy derivatives jump correspond to co-existence regions where the material undergoes a phase transition. In equation (8), ΔS and ΔV denote the change in the pure phase specific entropy and specific volume across the phase transition.

Points on the coexistence curve correspond to regions of non-strict convexity for the specific internal energy. In particular the Gibb's free energy is continuous across a coexistence curve, so that at a point (P,T) on such a curve we have:

$$-P\Delta V + T\Delta S = \Delta e. \tag{9}$$

As before Δe, ΔV, and ΔS denote the change in the corresponding quantity across the coexistence curve. Equation (8) follows by differentiating the expression $G_l(P,T) = G_g(P,T)$ with respect to temperature along the coexistence curve, where the subscripts denote the Gibb's free energies on either side of the curve (often regarded as a liquid and gaseos phase).

The key point in the above discussion is the equivalence of the equation of state formula in terms of a C^1 piecewise C^2 convex specific internal energy as a function of specific volume and specific entropy and the formulation of a piecewise C^2 strictly concave Gibb's free energy as a function of pressure and temperature (note the Gibb's free energy may not be continuously differentiable although left and right partial derivatives always exist). Indeed given such a Gibb's free energy, the specific internal energy is recovered via the Legendre transform:

$$e\left(V,S\right) = \sup_{(P,T)\in\Omega_{P,T}} \left\{G\left(P,T\right) - PV + TS\right\}. \tag{10}$$

It is precisely the assumption of convexity and lower semi-continuity of $e(V,S)$ or strict concavity and upper semi-continuity of $G(P,T)$ that implies the invertability of the Legendre transform between the specific internal and Gibb's free energies (again see reference [21] for details).

We finish this section by noting that the specific entropy relation as a function of specific volume and specific internal energy can also be inverted. Indeed, since

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}e + \frac{P}{T}\mathrm{d}V, \tag{11}$$

we can form the Legendre transform:

$$\sup_{(V,e)\in\Omega_{V,e}} \left\{\frac{TS(V,e) - e - PV}{T}\right\} = -\frac{1}{T}\inf_{(V,S)\in\Omega_{V,s}} \left\{e(V,S) + PV - TS\right\}$$

$$= -\frac{G(P,T)}{T}. \tag{12}$$

We can then recover $S(V,e)$ using the inverse Legendre transform:

$$S(V,e) = \inf_{(P,T)\in\Omega_{P,T}} \left\{\frac{e + PV - G(P,T)}{T}\right\}. \tag{13}$$

These relations are important in establishing the uniqueness of the pressure-temperature equilibrium solution below.

For later use, we also define the isothermal compressibility K_T, the isentropic compressibility K_S, the coefficient of thermal expansion β, and the specific heat at constant pressure C_P by the formulas:

$$K_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T, \quad K_S = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_s, \quad \beta = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P, \quad C_P = T\left.\frac{\partial S}{\partial T}\right|_P. \tag{14}$$

In appendix A of Menikoff and Plohr [18] a variety of useful relations between these quantities are listed. In particular the relations:

$$\frac{K_S}{K_T} = 1 - \frac{\beta^2 VT}{C_P K_T} = \frac{C_V}{C_P}, \quad \left.\frac{\partial S}{\partial V}\right|_T = \frac{\beta}{K_T}\Gamma = \frac{\beta V}{C_V K_T}, \quad K_S = \frac{1}{\rho c^2} \tag{15}$$

will prove useful in the sequel. The thermodynamic stability condition can be expressed in terms of the compressibilities and specific heats as:

$$C_P \geq C_V \geq 0 \quad \text{or} \quad K_T \geq K_S \geq 0. \tag{16}$$

3   Equilibrium Mixtures

Equilibrium mixtures can be characterized by the existence of a thermodynamic free energy as a function of two thermodynamic variables and parameterized by the component mass fractions. Such free energies might include a Gibb's free energy as a function of pressure and temperature or a Helmholtz free energy as a function of temperature and specific volume. The existence of a free energy means that the flow has a well defined temperature and entropy. Since mass fraction is advected with a non-reacting flow (an easy consequence of conservation of componnet mass), the thermodynamics of the mixture is essentially the same as described in section 2 in fluid elements that move with the flow. In particular the flow has a single acoustic sound speed. The assumption of an equilibrium mixture implies that the time scales of the process that establish the equilibrium (e.g. acoustic interactions or thermal conduction) are short relative to the dynamic time scales of interest. This assumption may often be inappropriate, so the use of equilibrium equation of state models are problem dependent. Nevertheless such models are very popular in application codes, and carry the benefit of considerable simplicity compared with non-equilibrium models.

In general the free energy of a mixture can be a complicated function of all of the component material properties (see for example [4]). In practice however, many applications only consider mixtures whose free energies can be described simply in terms of the free energies of the separate components, usually as a mass or volume average of the component free energies. Often such a formulation can be interpreted as a linearization with respect to mass fractions of a more complex non-linear function of the component free energies. In this section we describe two of the most popular equilibrium models in common usage.

3.1   Molecular Mixtures

The volume separated mix models to be described below allow for components to consist of molecularly mixed subcomponents. Molecular mixing is generally appropriate for gases or

miscible fluids and assume that mass diffusion occurs quickly compared to the flow dynamics and are generally useful for relatively slow flows. In particular shock dynamic processes are likely to violate the assumption of volume equilibrium used in this model. A mixture is said to be molecularly mixed if all components of the mixture occupy the same volume element simultaneously and are in temperature equilibrium with the mixture. Mathematically, this implies that all components have the same temperature, T, and that the mass density of a component is related to the mass density of the mixture via the relation $\rho_k = \mu_k \rho$ where μ_k is the mass fraction of species k, $1 \leq k \leq N$ for a mixture of N pure material components. In terms of specific volumes, this relation becomes $V = \mu_k V_k$. If we further assume that each component satisfies its pure material equation of state relative to its specific volume and temperature, then additivity of energy implies that the specific internal energy of the mixture is related to the specific internal energies of the components by the equation:

$$e(V, S, \vec{\mu}) = \sum_{k=1}^{N} \mu_k e_k(V_k, S_k),$$

$$\mu_k V_k = V, \quad T_k(V_k, S_k) = T, \quad S = \sum_{k=1}^{N} \mu_k S_k. \tag{17}$$

Obviously the thermodynamic domain of the mixture is a subset of the intersection of the domains of all of the components. Equation (17) can be expressed more directly in terms of additivity of the Helmholz free energy:

$$F(V, T, \vec{\mu}) = \sum_{k=1}^{N} \mu_k F_k(V_k, T). \tag{18}$$

It is a straightforward to show the two formulations are equivalent (although the equivalence even for phase transitions is slightly more complicated to prove) and that the mixture satisfies the thermodynamic relations:

$$\mathrm{d}e = T\mathrm{d}S - P\mathrm{d}V + \sum_{k=1}^{N} G_k \mathrm{d}\mu_k,$$

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \sum_{k=1}^{N} G_k \mathrm{d}\mu_k, \tag{19}$$

$$\mu_k V_k = V, \quad P = \sum_{k=1}^{N} P_k(V_k, T), \quad S = \sum_{k=1}^{N} \mu_k S_k(V_k, T), \quad G_k = G_k(P_k, T).$$

Here G_k is the Gibb's free energy of the k-th component. We note that here and in the sequel below we ignore the entropy of mixing, so that the total specific entropy is the mass average of the component values. This assumption is somewhat unrealistic in that it implies a certain unphysical reversability of the mixing process. For a more complete description of this issue see the book of Bird, Stewart, and Lightfoot [4].

In practice, the mixture equation of state will likely be computed by solving a system of equations. For example in the molecular mix case, given a specific internal energy e_k and specific volume V_k we would solve for the mixture pressure and temperature via one or the

other of the equivalent systems:

$$\begin{cases} V = \mu_k V_k(P_k, T_k), \quad k = 1, \cdots, N, \\ e = \sum_{k=1}^{N_k} \mu_k e_k(P_k, T), \end{cases} \quad \text{or} \quad \begin{cases} P_k = P_k\left(\dfrac{V}{\mu_k}, T\right), \quad k = 1, \cdots, N, \\ e = \sum_{k=1}^{N_k} \mu_k e_k\left(\dfrac{V}{\mu_k}, T\right). \end{cases} \tag{20}$$

Here $C_V = T\left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial e}{\partial T}\right|_V$ is the specific heat at constant volume, for mixtures these derivatives are also taken at constant mass fraction.

Thermodynamic derivatives of the mixture can then be computed in terms of the component values as follows:

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_{V,\vec{\mu}} = \sum_{k=1}^{N} \mu_k C_{V,k},$$

$$V\left.\frac{\partial P}{\partial V}\right|_{T,\vec{\mu}} = \sum_{k=1}^{N} V\left.\frac{\partial P_k}{\partial V_k}\right|_T \left.\frac{\partial V_k}{\partial V}\right|_{T,\vec{\mu}} = \sum_{k=1}^{N} V_k\left.\frac{\partial P_k}{\partial V_k}\right|_T \Rightarrow \frac{1}{K_T} = \sum_{k=1}^{N} \frac{1}{K_{T,k}}, \tag{21}$$

$$\left.\frac{\partial S}{\partial V}\right|_{T,\vec{\mu}} = \sum_{k=1}^{N} \mu_k\left.\frac{\partial S_k}{\partial V_k}\right|_T \left.\frac{\partial V_k}{\partial V}\right|_{T,\vec{\mu}} = \sum_{k=1}^{N} \left.\frac{\partial S_k}{\partial V_k}\right|_T \Rightarrow \frac{\beta}{K_T} = \sum_{k=1}^{N} \frac{\beta_k}{K_{T,k}}.$$

Equation (21) can then be used to compute the sound speed and Grüneisen exponents of the mixture:

$$\Gamma = \frac{V\beta}{C_V K_T} = \frac{1}{C_V}\sum_{k=1}^{N} \mu_k \frac{V_k \beta_k}{K_{T,k}} = \frac{1}{C_V}\sum_{k=1}^{N} \mu_k C_{V,k}\Gamma_k, \tag{22}$$

$$\rho c^2 = \frac{1}{K_S} = \frac{1}{K_T} + \Gamma\frac{\beta T}{K_T} = \frac{1}{K_T} + \Gamma^2\frac{C_V T}{V} \Rightarrow \tag{23}$$

$$c^2 = \sum_{k=1}^{N} \mu_k c_k^2 + \sum_{k=1}^{N} \mu_k \left(\Gamma^2 - \Gamma_k^2\right) C_{V,k}T,$$

$$C_P = C_V + \frac{\beta^2 VT}{K_T}. \tag{24}$$

From the formulas for the mixture isothermal compressibility and specific heat at constant volume, we see that the sound speed of the mixture is real if all of the components satisfy the thermodynamic stability constraints separately. It is also useful to derive a relation between changes in mixture pressure, mixture entropy, mixture specific volume, and mass fractions. Using equation (17) or (18) and the above identities, we find that:

$$dP = -\rho^2 c^2 dV + \rho\Gamma T dS + \rho^2 c^2 \sum_{k=1}^{N} \left.\frac{\partial G_k}{\partial P}\right|_{S,\vec{\mu}} d\mu_k. \tag{25}$$

The wave structure of the mixture is governed by the fundamental derivative of gas dynamics [35]:

$$\mathcal{G} = \frac{1}{2}\frac{V^2}{\rho c^2}\left.\frac{\partial^2 P}{\partial V^2}\right|_{S,\vec{\mu}} = -\frac{1}{2}\frac{(\rho c^2)^2}{V}\left.\frac{\partial^2 V}{\partial P^2}\right|_{S,\vec{\mu}}. \tag{26}$$

Shock waves are compressive in domains of thermodynamic phase space with $\mathcal{G} > 0$, while shocks that encompass domains with $\mathcal{G} < 0$ are expansive. A bit of algebra shows that the

fundamental derivative of gas dynamics can be written in terms of the Helmholtz free energy as:

$$\mathcal{G} = -\frac{1}{2}\frac{V^3}{c^2}\left[\frac{\partial^3 F}{\partial V^3} - 3\frac{\Gamma T}{V}\frac{\partial^3 F}{\partial V^2 \partial T} + 3\left(\frac{\Gamma T}{V}\right)^2 \frac{\partial^3 F}{\partial V \partial T^2} - \left(\frac{\Gamma T}{V}\right)^3 \frac{\partial^3 F}{\partial T^3}\right]. \tag{27}$$

It is an open question as to whether mixtures of materials with positive fundamental derivatives have positive fundamental derivatives, although to the authors' knowledge no counter-examples have been demonstrated.

3.2   Pressure-Temperature Equilibrium

In addition to molecular mix, another popular assumption for well mixed compositions is pressure temperature equilibrium, in which the components occupy disjoint volumes at the same temperature and pressure inside the microstructure. In this model, the volume fractions α_k, mass fractions, component densities and specific volumes, total density, and total specific volume are related by the formulas:

$$\alpha_k \rho_k = \mu_k \rho, \text{ or } \alpha_k V = \mu_k V_k. \tag{28}$$

The specific internal energy of the mixture is then given by:

$$e(V, S, \vec{\mu}) = \sum_{k=1}^{N} \mu_k e_k(V_k, S_k), \tag{29}$$

$$P_k(V_k, S_k) = P, \quad T_k(V_k, S_k) = T, \quad V = \sum_{k=1}^{N} \mu_k V_k, \quad S = \sum_{k=1}^{N} \mu_k S_k, \tag{30}$$

or more directly in terms of the Gibb's free energies:

$$G(P, T, \vec{\mu}) = \sum_{k=1}^{N} \mu_k G_k(P, T). \tag{31}$$

As with the molecular mix, most often, one would evaluate the P-T equilibrium equation of state using a numerical solution of a system of equations, in this case:

$$\begin{cases} V = \sum_{k=1}^{N} \mu_k V_k\,(P, T), \\ e = \sum_{k=1}^{N} \mu_k e_k\,(P, T), \end{cases} \quad \text{or} \quad \begin{cases} P = P_k\,(V_k, T), \quad k = 1, \cdots, N, \\ e = \sum_{k=1}^{N} \mu_k e_k\,(V_k, T). \end{cases} \tag{32}$$

Thermodynamic derivatives of the mixture can then be found using the formulas:

$$\begin{aligned} & C_P = \sum_{k=1}^{N} \mu_k C_{P,k}, \quad \alpha_k = \mu_k \frac{V_k}{V}, \; K_T = \sum_{k=1}^{N} \alpha_k K_{T,k}, \quad \beta = \sum_{k=1}^{N} \alpha_k \beta_k, \\ & \frac{1}{\Gamma} = -\beta T + \frac{K_T C_P}{\beta V}, \quad C_V = C_P - \frac{\beta^2 V T}{K_T}, \\ & -\frac{1}{\rho^2 c^2} = -V K_T + \frac{(\beta V)^2 T}{C_P}, \quad \frac{\Gamma^2 T}{c^2} = \frac{1}{C_V} - \frac{1}{C_P}. \end{aligned} \tag{33}$$

It is immediately obvious that the mixture specific heat at constant pressure and isothermal compressibility are non-negative if all of the component values are non-negative. The non-negativity of the specific heat at constant volume and the square of the sound speed are not

so obvious however. In fact this follows from general principles since the mixture Gibb's free energy is a convex (mass weighted) average of the concave functions $G_k(P,T)$ and hence is a concave function of pressure and temperature for fixed mass fractions. Moreover we have the stronger statement:

$$C_V \geq \sum_{k=1}^{N} \mu_k C_{V,k}. \tag{34}$$

Indeed:

$$C_V = C_P - \frac{\beta^2 VT}{K_T} = \sum_{k=1}^{N} \mu_k C_{V,k} + \sum_{k=1}^{N} \mu_k \frac{(\beta_k V_k)^2 T}{V_k K_{T,k}} - \frac{(\beta V)^2 T}{V K_T}. \tag{35}$$

Thus inequality (34) is equivalent to:

$$\sum_{k=1}^{N} \mu_k \frac{(\beta_k V_k)^2}{V_k K_{T,k}} \geq \frac{(\beta V)^2}{V K_T}. \tag{36}$$

Since $V K_T = \sum\limits_{k=1}^{N} \mu_k V_k K_{T,k}$ and $\beta V = \sum\limits_{k=1}^{N} \mu_k \beta_k V_k$, inequality (36) can be rewritten as:

$$\left| \sum_{k=1}^{N} \mu_k (V_k K_{T,k})^{\frac{1}{2}} \frac{\beta_k V_k}{(V_k K_{T,k})^{\frac{1}{2}}} \right| \leq \left(\sum_{k=1}^{N} \mu_k V_k K_{T,k} \right)^{\frac{1}{2}} \left(\sum_{k=1}^{N} \mu_k \frac{(\beta_k V_k)^2}{V_k K_{T,k}} \right)^{\frac{1}{2}},$$

which is a consequence of Schwartz's inequality.

The pressure, specific volume, entropy, and mass fraction evolution are related by the equation:

$$dP = -\rho^2 c^2 dV + \rho \Gamma T dS + \rho^2 c^2 \sum_{k=1}^{N} \left. \frac{\partial G_k}{\partial P} \right|_{S,\vec{\mu}} d\mu_k. \tag{37}$$

We note that (37) is formally identical to (25), however for P-T equilibrium we compute:

$$
\begin{aligned}
\rho^2 c^2 \left. \frac{\partial G_k}{\partial P} \right|_{S,\vec{\mu}} &= \rho^2 c^2 \left[V_k - S_k \left. \frac{\partial T}{\partial P} \right|_{S,\vec{\mu}} \right] = \rho^2 c^2 V_k + S_k \left. \frac{\partial T}{\partial V} \right|_{S,\vec{\mu}}, \\
\rho^2 c^2 \left. \frac{\partial G_k}{\partial P} \right|_{\rho^2 c^2} &= - \left. \frac{\partial G_k}{\partial V} \right|_{S,\vec{\mu}} = \rho^2 c^2 V_k - \rho \Gamma T S_k.
\end{aligned}
\tag{38}
$$

Finally we note that molecular mix is generally a "stronger" mix than P-T equilibrium, in the sense that it has a higher entropy at a given mixture pressure and temperature. Indeed at a given mixture pressure and temperature, the specific entropies are given by:

$$
\begin{aligned}
S_{PT} &= \sum_{k=1}^{N} \mu_k S_k(P,T), \quad P = P_k, \\
S_{MM} &= \sum_{k=1}^{N} \mu_k S_k(P_k, T), \quad P = \sum_{k=1}^{N} P_k.
\end{aligned}
\tag{39}
$$

If we assume non-negative pressures for all of the components, then for molecular mix $P_k \leq P$ and since $\left. \frac{\partial S_k}{\partial P_k} \right|_T = -\beta_k V_k = -\Gamma_k C_{V,k} K_{T,k}$, we have that for mixtures of components with non-negative coefficients of thermal expansion (equivalently non-negative Grüneisen exponents) $S_{MM} \geq S_{PT}$. Physically, molecular mix might be interpreted as a solution of all components

into a common medium, while P-T equilibrium mixtures might be thought of an emulsion of the components.

We can also compute the fundamental derivative for a P-T equilibrium mixture in terms of derivatives of the Gibb's free energy:

$$\mathcal{G} = \frac{1}{2} \frac{(\rho c^2)^3}{c^2} \left[\frac{\partial^3 G}{\partial P^3} + 3 \frac{\beta TV}{C_P} \frac{\partial^3 G}{\partial P^2 \partial T} + 3 \left(\frac{\beta TV}{C_P} \right)^2 \frac{\partial^3 G}{\partial P \partial T^2} + \left(\frac{\beta TV}{C_P} \right)^3 \frac{\partial^3 G}{\partial T^3} \right].$$

As for the molecular mix case, it is an open question whether P-T equilibrium mixtures of components with positive fundamental derivatives also have a positive fundamental derivative. One should note that while for a pure material, the fundamental derivative can be computed using only incomplete equation of state information:

$$\mathcal{G} = \frac{1}{2} V \left[\left. \frac{\partial P}{\partial e} \right|_V + \left(\frac{PV}{c} \right)^2 \left. \frac{\partial^2 P}{\partial e^2} \right|_V - 2 \left(\frac{PV}{c} \right) \left(\frac{V}{c} \right) \frac{\partial^2 P}{\partial e \partial V} + \left(\frac{V}{c} \right)^2 \left. \frac{\partial^2 P}{\partial V^2} \right|_e \right],$$

$$\rho^2 c^2 = \frac{c^2}{V^2} = P \left. \frac{\partial P}{\partial e} \right|_V - \left. \frac{\partial P}{\partial V} \right|_e,$$

(40)

the pressure-temperature equilibrium mixture fundamental derivative depends on the complete equations of state of all of the components.

4   Basic Pressure-Velocity equilibrium Mix Model

We will now examine classes of hydrodynamic models that can be used to describe non-temperature equilibrium flows that maintain a single mixture pressure and velocity. In smooth flow regions each species' entropy is advected by the common velocity and modified by interactions via P-V work between materials. Following the notation of Drew and Passman [7], the system is written:

$$\frac{\partial \alpha_k \rho_k}{\partial t} + \nabla \bullet (\alpha_k \rho_k \mathbf{u}) = \alpha_k \rho_k R_k = \rho \mu_k R_k,$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \bullet (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla P = \rho \mathbf{b},$$

$$\frac{\partial \rho \left(e + \frac{1}{2} u^2 \right)}{\partial t} + \nabla \bullet \rho \mathbf{u} \left(e + \frac{1}{2} u^2 \right) + \nabla \bullet P \mathbf{u} = \rho \mathbf{b} \bullet \mathbf{u} + \rho q,$$

$$T_k \frac{DS_k}{Dt} = \frac{De_k}{Dt} + P \frac{DV_k}{Dt} = Q_k.$$

(41)

Here α_k is the k-th material species volume fraction, $1 \leq k \leq N$, ρ_k is the component micro-density of this species, $\mathbf{u}$ is the fluid velocity, $\rho = \sum_{k=1}^{N} \alpha_k \rho_k$ is the total fluid density, P is the equilibrium pressure, $\mathbf{b}$ is a body force per unit mass, Q_k is the heat production in species k due to interactions between species and external sources, q is the total heat production for the mixture due to interactions and external sources, $\mu_k = \alpha_k \rho_k / \rho$, T_k and S_k are the mass fraction, temperature, and specific entropy of species k, and $\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u} \bullet \nabla$ is the total derivation operator. We allow for the production or destruction of a particular species via the reaction source terms $\alpha_k \rho_k R_k$. For simplicity we assume the flow is saturated, $\sum_{k=1}^{N} \alpha_k = 1$

and that total mass is conserved so that $\sum_{k=1}^{N} \mu_k R_k = 0$. The first three equations correspond to the conservation of individual material mass, total momentum, and total energy, while the last equation is the advection law for the separate specific entropies. The internal energies, temperatures, and specific entropies are related by separate thermodynamic equations of state described in Section 2.

More generally we can assume that each species is either a miscible (molecularly mixed) mixture of subcomponent materials or an immiscible pressure-temperature mixture of subcomponents. This extension is straightforward; the species micro-density is then a combination

$$\rho_k = \sum_{i=1}^{N_k} \alpha_{ki} \rho_{ki}, \tag{42}$$

where α_{ki} is the sub-volume fraction of a subcomponent with respect to the volume occupied by the mixture. The sub-mass fractions are defined by $\mu_{ki} \rho_k = \alpha_{ki} \rho_{ki}$. The conservation of subcomponent mass implies:

$$\frac{\partial \alpha_k \alpha_{ki} \rho_{ki}}{\partial t} + \nabla \bullet (\alpha_k \alpha_{ki} \rho_{ki} \mathbf{u}) = \alpha_k \alpha_{ki} \rho_{ki} R_{ki}. \tag{43}$$

The source term for the mixture $R_k = \sum_{i=1}^{N_k} \mu_{ki} R_{ki}$ is then the sum of the sources for the subcomponents of the mixture. It is important to note that the subcomponent volume fractions are constitutive properties of the subcomponent state (i.e., given by an equation of state as described in Section 3), while the component volume fractions require additional dynamical equations to describe their evolution.

Physically, system (41) is most reasonable in the case of weak shocks, say as measured by the pure material normal shock mach numbers. The hypothesis of pressure and velocity equilibrium is based on the assumption that the microstructure is "well-mixed", i.e., the subgrid scale structure of a mixed region is either molecularly mixed or has sufficiently convoluted subgrid interfaces to justify a mixed cell treatment with a single common pressure and velocity. Generally speaking, this means that the subgrid structure is likely composed of large numbers of droplets of individual materials. Treatments for mixtures that experience strong shocks, or for which the subgrid scale is not well mixed, will almost certainly require multiple species velocities and pressures. A discussion of such models is not the intent of this research note.

System (41) can be reformulated in a variety of ways. Summing the individual continuity equations over all materials we obtain the continuity equation for total mass:

$$\frac{\partial \rho}{\partial t} + \nabla \bullet \rho \mathbf{u} = \sum_{k=1}^{N} \alpha_k \rho_k R_k = 0, \tag{44}$$

which implies that mass fractions are advected with the component mass source:

$$\frac{D\mu_k}{Dt} = \mu_k R_k. \tag{45}$$

For mixture components, the subcomponent mass fractions are advected by the equations:

$$\frac{D\mu_k \mu_{ki}}{Dt} = \mu_{ki} \mu_k R_{ki}, \quad \frac{D\mu_{ki}}{Dt} = \mu_{ki} (R_{ki} - R_k), i = 1, \cdots, N_k. \tag{46}$$

If we take the individual material continuity equations and expand the derivatives, we obtain:

$$\alpha_k \frac{D\rho_k}{Dt} + \rho_k \frac{D\alpha_k}{Dt} + \alpha_k \rho_k \nabla \bullet \mathbf{u} = \alpha_k \rho_k R_k,$$

$$\frac{D\alpha_k}{Dt} = \alpha_k \left[\frac{1}{V_k} \frac{DV_k}{Dt} + R_k - \nabla \bullet \mathbf{u} \right]. \tag{47}$$

The pressure, micro-density, and entropy derivatives are related by the formulas (25)/(37), from which we obtain:

$$\frac{D\alpha_k}{Dt} + \alpha_k \left[\frac{1}{\rho_k c_k^2} \frac{DP}{Dt} - \frac{\Gamma_k T_k}{c_k^2} \frac{DS_k}{Dt} \right] + \alpha_k \nabla \bullet \mathbf{u}$$

$$= \alpha_k \left[R_k - \rho_k \sum_{i=1}^{N_k} \mu_{ki} \frac{\partial G_{ki}}{\partial P} \bigg|_{S_k, \vec{\mu}_{ki}} (R_{ki} - R_k) \right] \equiv \alpha_k \mathcal{R}_k. \tag{48}$$

If we use the relation $\nabla \bullet \mathbf{u} = \frac{1}{V} \frac{DV}{Dt}$ where $V = 1/\rho = \sum_{k=1}^{N} \mu_k V_k$ is the total specific volume, then equation (48) can be rewritten as:

$$\frac{D\alpha_k}{Dt} = \alpha_k \left(\frac{\Gamma_k T_k}{c_k^2} \frac{DS_k}{Dt} - \frac{1}{\rho_k c_k^2} \frac{DP}{Dt} - \frac{1}{V} \frac{DV}{Dt} + \mathcal{R}_k \right) = \alpha_k \left(\frac{1}{V_k} \frac{DV_k}{Dt} - \frac{1}{V} \frac{DV}{Dt} + \mathcal{R}_k \right). \tag{49}$$

Remark It is convenient to note at this point that the relation $\alpha_k V = \mu_k V_k(P, S_k)$, $V = \sum_{j=1}^{N} \mu_j V_j(P, S_j)$ can be used to derive the equation:

$$d\alpha_k = \frac{V_k}{V} d\mu_k - \sum_{j=1}^{N} \alpha_k \frac{V_j}{V} d\mu_j + \alpha_k \left[\sum_{j=1}^{N} \frac{\alpha_j}{\rho_j c_j^2} - \frac{1}{\rho_k c_k^2} \right] dP$$

$$+ \alpha_k \left[\frac{\Gamma_k T_k}{c_k^2} dS_k - \sum_{j=1}^{N} \alpha_j \frac{\Gamma_j T_j}{c_j^2} dS_j \right],$$

$$d\alpha_k = \sum_{j=1}^{N} \left(\alpha_j \frac{V_k}{V} d\mu_k - \alpha_k \frac{V_j}{V} d\mu_j \right) + \left[\sum_{j=1}^{N} \alpha_k \alpha_j \left(\frac{1}{\rho_j c_j^2} - \frac{1}{\rho_k c_k^2} \right) \right] dP$$

$$+ \sum_{j=1}^{N} \alpha_k \alpha_j \left(\frac{\Gamma_k T_k}{c_k^2} dS_k - \frac{\Gamma_j T_j}{c_j^2} dS_j \right). \tag{50}$$

It is straightforward to check from the velocity/pressure equilibrium Euler equations, that this model will be hyperbolic with a single acoustic speed c if the total derivatives of the equilibrated pressure and total specific volume are related by the equation:

$$\frac{DP}{Dt} + \rho^2 c^2 \frac{DV}{Dt} = \rho c^2 \mathcal{S},$$

$$\frac{De}{Dt} + P \frac{DV}{Dt} = q, \tag{51}$$

where $e = \sum_{k=1}^{N} \mu_k e_k$ is the total specific internal energy of the mixture and $\mathcal{S}$ and q are some yet to be specified source terms. (Remark: equation (51) is the assumption of a single sound speed; other hyperbolic assumptions could introduce multiple sound speeds. We do not consider such

models here, although they are critical in the analysis of flows that are not in pressure and velocity equilibrium.)

Substituting equation (51) into equation (49) we get:

$$\frac{D\alpha_k}{Dt} = \alpha_k \frac{\Gamma_k}{c_k^2} T_k \frac{DS_k}{Dt} + \alpha_k \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \right] \frac{DP}{Dt} + \alpha_k \left(\mathcal{R}_k - \mathcal{S} \right). \tag{52}$$

Equation (52) suggests a family of models where both volume fraction and entropy advection are proportional to pressure advection. Without loss of generality, such models can be written in the form:

$$\begin{aligned}
T_k \frac{DS_k}{Dt} = Q_k = -\frac{c_k^2}{\Gamma_k} \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \right] \left(\frac{1 - \delta_k}{2} \right) \frac{DP}{Dt} + q_k, \\
\frac{D\alpha_k}{Dt} = \alpha_k \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \right] \left(\frac{1 + \delta_k}{2} \right) \frac{DP}{Dt} + \alpha_k \left(\frac{\Gamma_k}{c_k^2} q_k + \mathcal{R}_k - \mathcal{S} \right).
\end{aligned} \tag{53}$$

The quantities $\delta_k = \delta_k(e, V, \vec{\alpha}, \vec{\mu})$ and q_k are modeling terms that are in general complicated functions (for example see equation (87) for pressure temperature equilibrium) of the thermodynamic flow state or even given by separate dynamic equations. However we will treat these terms as if they were "pure" source terms (i.e., do not contain derivatives) as might be appropriate when treating the evolution of these terms separately using operator splitting. For example, in the sequel q_k can include heat conduction and radiation heat sources that produce parabolic modifications of the basic conservation laws.

The mix model terms δ_k govern the degree to which pressure advection changes either heat ($T\mathrm{d}S$ terms) or volume fraction. When δk is close to one, pressure advection largely drives relative volumetric changes in the flow components while for δ_k close to minus one the main contribution of pressure advection is the change to heat.

It is reasonable to assume that the total heat source is the mass average of the species heat sources, so we define

$$q \equiv \sum_{k=1}^{N} \mu_k Q_k. \tag{54}$$

Examining the first of equations (53) we see that if the composite sound speed is to be independent of the heat sources, we require:

$$\mathcal{S} = \sum_{k=1}^{N} \alpha_k \left(\frac{\Gamma_k q_k}{c_k^2} + \mathcal{R}_k \right). \tag{55}$$

With these assumptions (51) becomes:

$$\begin{aligned}
\frac{DP}{Dt} + \rho^2 c^2 \frac{DV}{Dt} = \rho c^2 \mathcal{S} = \rho c^2 \sum_{k=1}^{N} \alpha_k \left(\frac{\Gamma_k q_k}{c_k^2} + \mathcal{R}_k \right), \\
\frac{De}{Dt} + P \frac{DV}{Dt} = q = \sum_{k=1}^{N} \mu_k Q_k = \sum_{k=1}^{N} \mu_k q_k.
\end{aligned} \tag{56}$$

Taking the mass average of the first of equations (53) and summing the second gives two

formulas for the composite bulk modulus ρc^2:

$$\rho c^2 \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k} \left(\frac{1-\delta_k}{2}\right) = \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k} \left(\frac{1-\delta_k}{2}\right) \rho_k c_k^2,$$

$$\frac{1}{\rho c^2} \sum_{k=1}^{N} \alpha_k \left(\frac{1+\delta_k}{2}\right) = \sum_{k=1}^{N} \alpha_k \left(\frac{1+\delta_k}{2}\right) \frac{1}{\rho_k c_k^2}. \tag{57}$$

The compatibility condition on the mix model terms δ_k thus is:

$$\left[\sum_{k=1}^{N} \alpha_k \left(\frac{1+\delta_k}{2}\right)\right] \left[\sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k} \left(\frac{1-\delta_k}{2}\right)\right] = \left[\sum_{k=1}^{N} \frac{\alpha_k}{\rho_k c_k^2} \left(\frac{1+\delta_k}{2}\right)\right] \left[\sum_{k=1}^{N} \alpha_k \frac{\rho_k c_k^2}{\Gamma_k} \left(\frac{1-\delta_k}{2}\right)\right]. \tag{58}$$

Equation (57) shows that for $-1 < \delta_k < 1$ both the bulk modulus and its reciprocal are convex combinations of the component values, while for $\delta_k = 1$, the reciprocal bulk modulus is a convex combination of the component values and for $\delta_k = -1$ the bulk modulus is given by a convex combination of the component values. Actually, these are convex combinations only for the case where the Grüneisen exponents are positive, something that need not be true in general. However this quantity if usually positive for most materials of interest, and we will always assume in the following that this is the case for the equations of state being considered. In particular we have that the mixture sound speed is real if all of the component sound speeds are real and $-1 \leq \delta_k \leq 1$. We also observe that constraint (58) implies that there is a $N - 1$ dimensional family of possible model terms, i.e., specifying functional forms or any subset of $N - 1$ of these quantities determines the remaining one.

If we combine the second of equation (56) with the conservation laws of total mass and momentum, we obtain a conservation law for total energy:

$$\frac{\partial \left[\rho \left(e + \frac{1}{2} u^2\right)\right]}{\partial t} + \nabla \bullet \left[\rho \mathbf{u} \left(e + \frac{1}{2} u^2\right) + P \mathbf{u}\right] = \rho \mathbf{u} \bullet \mathbf{b} + \rho q. \tag{59}$$

We will henceforth regard (59) as a fundamental conservation law. We thus can rewrite system (41) as the equivalent system:

Conservation of Subcomponent Mass:

$$\frac{\partial \alpha_k \alpha_{ki} \rho_{ki}}{\partial t} + \nabla \bullet (\alpha_k \alpha_{ki} \rho_{ki} \mathbf{u}) = \alpha_k \alpha_{ki} \rho_{ki} R_{ki}, \quad i = 1, \cdots, N_k. \tag{60}$$

Conservation of Component Mass:

$$\frac{\partial \alpha_k \rho_k}{\partial t} + \nabla \bullet (\alpha_k \rho_k \mathbf{u}) = \alpha_k \rho_k R_k,$$

$$\frac{\partial \alpha_k \rho_k}{\partial t} + \nabla \bullet (\alpha_k \rho_k \mathbf{u}) = \sum_{i=1}^{N_k} \left(\frac{\partial \alpha_k \alpha_{ki} \rho_{ki}}{\partial t} + \nabla \bullet (\alpha_k \alpha_{ki} \rho_{ki} \mathbf{u})\right), \tag{61}$$

$$\alpha_k \rho_k R_k = \sum_{i=1}^{N_k} \alpha_k \alpha_{ki} \rho_{ki} R_{ki}.$$

Conservation of Total Mass:

$$\frac{\partial \rho}{\partial t} + \nabla \bullet (\rho \mathbf{u}) = 0,$$

$$\frac{\partial \rho}{\partial t} + \nabla \bullet (\rho \mathbf{u}) = \sum_{k=1}^{N} \frac{\partial \alpha_k \rho_k}{\partial t} + \nabla \bullet (\alpha_k \rho_k \mathbf{u}), \tag{62}$$

$$\sum_{k=1}^{N} \alpha_k \rho_k R_k = 0.$$

Conservation of Total Momentum:

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \bullet (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla P = \rho \mathbf{b}. \tag{63}$$

Conservation of Total Energy:

$$\frac{\partial \left[\rho \left(e + \frac{1}{2}u^2\right)\right]}{\partial t} + \nabla \bullet \left[\rho \mathbf{u}\left(e + \frac{1}{2}u^2\right) + P\mathbf{u}\right] = \rho \mathbf{u} \bullet \mathbf{b} + \rho q. \tag{64}$$

Heat/Volume Advection:

$$T_k \frac{DS_k}{Dt} = \frac{De_k}{Dt} + P\frac{DV_k}{Dt} = \frac{V_k}{\Gamma_k}\left[\rho_k c_k^2 - \rho c^2\right]\left(\frac{1-\delta_k}{2}\right)(\nabla \bullet \mathbf{u} - \mathcal{S}) + q_k,$$

$$\frac{D\alpha_k}{Dt} = -\alpha_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2}\right]\left(\frac{1+\delta_k}{2}\right)(\nabla \bullet \mathbf{u} - \mathcal{S}) + \alpha_k \left(\frac{\Gamma_k}{c_k^2}q_k + \mathcal{R}_k - \sum_{j=1}^{N}\alpha_j\left(\frac{\Gamma_j q_j}{c_j^2} + \mathcal{R}_j\right)\right). \tag{65}$$

System (60)–(65) explicitly expresses conservation of mass, momentum, and energy and implicitly the advection of entropy and/or volume fraction.

The above derivations allows to us to derive the alternate formulation of system (41) from which the characteristic analysis is easily derived:

$$\frac{D\mu_k}{Dt} = \mu_k R_k, \frac{D\mu_{ki}}{Dt} = \mu_{ki}(R_{ki} - R_k),$$

$$T_k \frac{DS_k}{Dt} = -\frac{c_k^2}{\Gamma_k}\left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2}\right]\left(\frac{1-\delta_k}{2}\right)\frac{DP}{Dt} + q_k,$$

$$\frac{DP}{Dt} + \rho c^2 \nabla \bullet \mathbf{u} = \rho c^2 \mathcal{S}, \tag{66}$$

$$\frac{D\mathbf{u}}{Dt} + \frac{\nabla P}{\rho} = \mathbf{b}.$$

System (66) is equivalent to the system in terms of the volume fractions:

$$\frac{D\mu_k}{Dt} = \mu_k R_k, \frac{D\mu_{ki}}{Dt} = \mu_{ki}(R_{ki} - R_k),$$

$$\frac{D\alpha_k}{Dt} = \alpha_k \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2}\right]\left(\frac{1+\delta_k}{2}\right)\frac{DP}{Dt} + \alpha_k \left(\frac{\Gamma_k}{c_k^2}q_k + \mathcal{R}_k - \mathcal{S}\right),$$

$$\frac{DP}{Dt} + \rho c^2 \nabla \bullet \mathbf{u} = \frac{DP}{Dt} + \rho^2 c^2 \frac{DV}{Dt} = \rho c^2 \mathcal{S}, \tag{67}$$

$$\frac{De}{Dt} + P\frac{DV}{Dt} = q,$$

$$\frac{D\mathbf{u}}{Dt} + \frac{\nabla P}{\rho} = \mathbf{b}.$$

Either of the versions in systems (66) or (67) imply that if the heat and reaction terms are either defined as constitutive functions of the flow state, or are determined by independent dynamically equations (not involving state derivatives), then such a model has $2N + D - 1$ linearly degenerate eigenvalues with characteristic speed $\lambda = \mathbf{u} \bullet \xi$ in the direction of the unit vector ξ, and two wave families with speeds $\lambda = \mathbf{u} \bullet \xi \pm c$.

4.1   Constitutive Laws

If we assume that the reaction terms R_k, R_{ki}, the heat sources q_k, and the mix model coefficients δ_k are either constitutive functions of flow state (microdensities, pressure, volume fractions, mass fractions, temperatures, or equivalent) or are given by additional dynamical equations not being considered here, and that each component is a mixture of $N_k, k = 1, \cdots, N$, then system (60)–(65) or its characteristic forms (66) or (67) consist of $\sum\limits_{k=1}^{N} N_k + N + D$ independent dynamic equations (Table 1). Here D is the spatial dimension of the flow.

Table 1   Partial Differential Equation Count

System (60)–(65)

Quantity	Number of Independent Equations
Species Mass	$\sum\limits_{k=1}^{N} N_k$
Momentum	D
Total Energy	1
Species Heat/Volume Fraction	$N - 1$
Total	$\sum\limits_{k=1}^{N} N_k + N + D$

System (66)

Quantity	Number of Independent Equations
Species Mass Fraction	$N - 1$
Subspecies Mass Fraction	$\sum\limits_{k=1}^{N} N_k - N$
Species Heat	N
Pressure Advection	1
Velocity	D
Total	$\sum\limits_{k=1}^{N} N_k + N + D$

System (67)

Quantity	Number of Independent Equations
Species Mass Fraction	$N - 1$
Subspecies Mass Fraction	$\sum\limits_{k=1}^{N} N_k - N$
Species Volume Fraction	$N - 1$
Pressure Advection	1
Specific Internal Energy Advection	1
Velocity	D
Total	$\sum\limits_{k=1}^{N} N_k + N + D$

The variables used to specify the flow are described in Table 2.

<div align="center">

Table 2   Flow State Specification Variables

</div>

Variable Type	Names	Count/Number
Subspecies Thermodynamic State	$T_{ki}, P_{ki}, \rho_{ki}, e_{ki}, S_{ki},$	$2\sum_{k=1}^{N} N_k$
Species Mass Fraction	μ_k	$N-1$
Sub-species Mass Fraction	μ_{ki}	$\sum_{k=1}^{N} N_k - N$
Species Volume Fraction	α_k	$N-1$
Sub-species Volume Fraction	α_{ki}	$\sum_{k=1}^{N} N_k - N$
Species Total Density/Specific Volume	$\rho_k, V_k = \frac{1}{\rho_k}$	N
Species Specific Internal Energy	e_k	N
Species Pressure	P_k	N
Species Temperature	T_k	N
Total Density/Specific Volume	$\rho, V = \frac{1}{\rho}$	1
Total Specific Internal Energy	e	1
Total Pressure	P	1
Velocity	$\mathbf{u}$	D
Total		$4\sum_{k=1}^{N} N_k + 4N + D + 1$

From these two tables we see that we require an additional $3\sum_{k=1}^{N} N_k + 3N + 1$ equations to close the system. These equations are provided by the constitutive relations in described in Table 3.

<div align="center">

Table 3   Constitutive Closure Relations

</div>

Equation	Description	Count/Number
Total Energy	$e = \sum_{k=1}^{N} e_k$	1
Total/Species Mass	$\alpha_k \rho_k = \mu_k \rho$	N
Species/Sub-species Mass	$\alpha_{ki} \rho_{ki} = \mu_{ki} \rho_k$	$\sum_{k=1}^{N} N_k$
Species/Sub-species Specific Internal Energy	$e_k = \sum_{i=1}^{N_k} \mu_{ki} e_{ki}$	N
Sub-species Thermodynamic Equilibrium	Pressure/Temperature or	$2\sum_{k=1}^{N} N_k$
	Molecular Mix equilibrium	
	$P_{ki} = P_k, \quad T_{ki} = T_k$	
Single Pressure	$P = P_k$	N
Total		$3\sum_{k=1}^{N} N_k + 3N + 1$

An examination of our partial differential equation systems together with the constitutive closures shows that we basically need to compute the equilibrated pressure as a function of total density, mass fractions (species + subspecies), and either the species specific entropies, specific

internal energies, or volume fractions. The sub-species equilibrium assumptions imply that we can write the species pressure and specific internal energies in any one of several equivalent ways:

$$
\begin{aligned}
P_k &= P_k(V_k, S_k, \vec{\mu}_k = (\mu_{k1}, \cdots, \mu_{kN_k})) = P_k\Big(\frac{\alpha_k V}{\mu_k}, S_k, \vec{\mu}_k\Big), \\
e_k &= e_k V_k, S_k, \vec{\mu}_k) = e_k\Big(\frac{\alpha_k V}{\mu_k}, S_k, \vec{\mu}_k\Big),
\end{aligned}
\tag{68}
$$

$$
P_k = P_k(V_k, e_k, \vec{\mu}_k) = P_k\Big(\frac{\alpha_k V}{\mu_k}, e_k, \vec{\mu}_k\Big), \tag{69}
$$

$$
e_k = e_k(V_k, P_k, \vec{\mu}_k) = e_k\Big(\frac{\alpha_k V}{\mu_k}, P_k, \vec{\mu}_k\Big). \tag{70}
$$

The common pressure can be found as a solution in terms of the desired variables of the system of $N+1$ equations:

$$
\begin{aligned}
P &= P_k(\cdot), \\
e &= \sum_{k=1}^{N} \mu_k e_k.
\end{aligned}
\tag{71}
$$

If we further assume that the separate material equations of state can be expressed through an incomplete equation of state formulation, $P_k = P_k(V_k, e_k, \vec{\mu}_k)$, then system (71) becomes:

$$
\begin{aligned}
P &= P_k(V_k, e_k, \vec{\mu}_k) = P_k\Big(\frac{\alpha_k V}{\mu_k}, e_k, \vec{\mu}_k\Big), \quad k = 1, \cdots, N, \\
e &= \sum_{k=1}^{N} \mu_k e_k,
\end{aligned}
\tag{72}
$$

which yields a solution:

$$
\begin{aligned}
P &= P(V, e, \vec{\alpha}, \vec{\mu}), \\
e_k &= e_k(V, e, \vec{\alpha}, \vec{\mu}).
\end{aligned}
\tag{73}
$$

Newton's scheme provides one method to solve system (72), linearizing this system with respect to pressure and specific internal energy we obtain the iteration:

$$
\begin{aligned}
P^{n+1} &= \frac{\sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k^n} P_k^n}{\sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k^n}}, \quad P_k^n = P_k\left(V_k, e_k^n, \vec{\mu}_k\right), \quad \Gamma_k^n = \Gamma_k\left(V_k, e_k^n, \vec{\mu}_k\right), \\
e_k^{n+1} &= e_k^n + V_k \frac{P^{n+1} - P_k^n}{\Gamma_k^n} = e_k^n + V_k \frac{\Gamma^n}{\Gamma_k^n} \sum_{j=1}^{N} \frac{\alpha_j}{\Gamma_j^n} \left[P_j^n - P_k^n\right], \\
\frac{1}{\Gamma^n} &= \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k^n}.
\end{aligned}
\tag{74}
$$

System (74) shows that it is sufficient to solve for the component specific internal energies and then compute the common pressure using the average of the component pressures weighted by the ratio of the given volume fraction and Grüneisen exponent. The iteration can be started

using the initial guess $e_k^0 = e$, $k = 1, \cdots, N$. It is useful to note that if all of the components have equations of state of the Mie-Grüneisen type

$$P_k = P_{r,k}(V_k) + \frac{\Gamma_k(V_k)}{V_k}(e_k - e_{r,k}(V_k)), \tag{75}$$

then the linear relation between pressure and specific internal energy for fixed specific volume implies that the Newton method (74) converges to the exact solution:

$$
\begin{aligned}
P &= P_r(V, \vec{\alpha}, \vec{\mu}) + \frac{\Gamma(V, \vec{\alpha}, \vec{\mu})}{V}[e - e_r(V, \vec{\alpha}, \vec{\mu})], \\
e_k(V, \vec{\alpha}, \vec{\mu}) &= e_{r,k}(V_k) + \frac{V_k}{\Gamma_k(V_k)}[P - P_{r,k}(V_k)], \\
V_k &= \frac{\alpha_k V}{\mu_k}, \\
\frac{1}{\Gamma(V, \vec{\alpha}, \vec{\mu})} &= \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k(V_k)}, \\
P_r(V, \vec{\alpha}, \vec{\mu}) &= \Gamma(V, \vec{\alpha}, \vec{\mu}) \sum_{k=1}^{N} \frac{\alpha_k P_{r,k}(V_k)}{\Gamma_k(V_k)}, \\
e_r(V, \vec{\alpha}, \vec{\mu}) &= \sum_{k=1}^{N} \mu_k e_{r,k}(V_k),
\end{aligned}
\tag{76}
$$

in a single iteration. In practice equations of this type are extremely common (indeed analytic equations are almost always of this type), and in general the Grüneisen exponent tends to be slowly varying for fixed specific volume so one would expect that iteration (74) would usually converge quickly even for the most general equation of state mixtures.

It is convenient to compute the partial derivatives of the pressure solution of system (72). We leave it as an exercise to show that:

$$
\begin{aligned}
\left.\frac{\partial P}{\partial e}\right|_{V, \vec{\alpha}, \vec{\mu}} &= \rho\Gamma, \quad \frac{1}{\Gamma} = \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k}, \\
\left.\frac{\partial P}{\partial V}\right|_{e, \vec{\alpha}, \vec{\mu}} &= \rho\Gamma\left[P - \sum_{k=1}^{N} \frac{\alpha_k \rho_k c_k^2}{\Gamma_k}\right], \\
\left.\frac{\partial P}{\partial \alpha_k}\right|_{V, e, \alpha_{j \neq k}, \vec{\mu}} &= \Gamma\left[P - \frac{\rho_k c_k^2}{\Gamma_k}\right], \\
\left.\frac{\partial P}{\partial \mu_k}\right|_{V, e, \vec{\alpha}, \mu_{j \neq k}} &= -\rho\Gamma\left[e_k + V_k P - \frac{c_k^2}{\Gamma_k}\right].
\end{aligned}
\tag{77}
$$

Derivatives of the component specific internal energies, temperatures, and specific volumes can be derived from equation (77) using the relations:

$$
\begin{aligned}
\frac{dV_k}{V_k} + \frac{d\mu_k}{\mu_k} &= \frac{dV}{V} + \frac{d\alpha_k}{\alpha_k}, \\
de_k &= \left.\frac{\partial e_k}{\partial P}\right|_{V_k} dP + \left.\frac{\partial e_k}{\partial V_k}\right|_{P} dV_k = \frac{V_k}{\Gamma_k} dP + \left[\frac{c_k^2}{\Gamma_k} - PV_k\right]\frac{dV_k}{V_k} \\
dT_k &= \left.\frac{\partial T_k}{\partial P}\right|_{V_k} dP + \left.\frac{\partial T_k}{\partial V_k}\right|_{P} dV_k = \frac{V_k}{\Gamma_k C_{V,k}} dP + \frac{c_k^2 - \Gamma_k^2 C_{V,k} T_k}{\Gamma_k C_{V,k}}\frac{dV_k}{V_k}.
\end{aligned}
\tag{78}
$$

Equation (77) implies that the total derivative of the common pressure is given by:

$$\frac{DP}{Dt} = -\Gamma \sum_{k=1}^{N} \alpha_k \frac{\rho_k c_k^2}{\Gamma_k} \frac{1}{V} \frac{DV}{Dt} - \Gamma \sum_{k=1}^{N} \frac{\rho_k c_k^2}{\Gamma_k} \frac{D\alpha_k}{Dt},$$

$$\frac{DP}{Dt} + \Gamma \sum_{k=1}^{N} \frac{\rho_k c_k^2}{\Gamma_k} \Big(\frac{D\alpha_k}{Dt} + \alpha_k \nabla \cdot \mathbf{u} \Big) = 0. \tag{79}$$

5   Specific Models (single sound speed)

Flow equations of the form (60)–(65) include several popular multi-material flow models. Equation (58) implies that we have $N-1$ degrees of algebraic freedom in selecting parameters for models of this type. We will not pursue further possible models for the parameters δ_k except to note that this framework includes the pressure-temperature equilibrium flow model and points out an interesting duality between two popular multi-temperature models:

Uniform Strain

$$\delta_k = -1, \quad k = 1, \cdots, N,$$

$$\frac{D\alpha_k}{Dt} = \alpha_k \Big(\frac{\Gamma_k}{c_k^2} q_k + \mathcal{R}_k - \mathcal{S} \Big),$$

$$\frac{\Gamma_k}{c_k^2} T_k \frac{DS_k}{Dt} = -\Big[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \Big] \frac{DP}{Dt} + \frac{\Gamma_k}{c_k^2} q_k = \Big[1 - \frac{\rho c^2}{\rho_k c_k^2} \Big] \nabla \bullet \mathbf{v} + \frac{\Gamma_k}{c_k^2} q_k, \tag{80}$$

$$\rho c^2 = \frac{\sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k} \rho_k c_k^2}{\sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k}}.$$

Thermal Isolation

$$\delta_k = +1, k = 1, \cdots, N,$$

$$T_k \frac{DS_k}{Dt} = q_k,$$

$$\frac{D\alpha_k}{Dt} = \alpha_k \Big[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \Big] \frac{DP}{Dt} + \alpha_k \Big(\frac{\Gamma_k}{c_k^2} q_k + \mathcal{R}_k - \mathcal{S} \Big)$$

$$= \alpha_k \Big[\frac{\rho c^2}{\rho_k c_k^2} - 1 \Big] \nabla \bullet \mathbf{v} + \alpha_k \Big(\frac{\Gamma_k}{c_k^2} q_k + \mathcal{R}_k - \mathcal{S} \Big), \tag{81}$$

$$\frac{\partial \alpha_k}{\partial t} + \nabla \bullet (\alpha_k \mathbf{v}) = \alpha_k \frac{\rho c^2}{\rho_k c_k^2} \nabla \bullet \mathbf{v} + \alpha_k \Big(\frac{\Gamma_k}{c_k^2} q_k + \mathcal{R}_k - \mathcal{S} \Big),$$

$$\frac{1}{\rho c^2} = \sum_{k=1}^{N} \frac{\alpha_k}{\rho_k c_k^2}.$$

One immediate observation of equation (80) is that the uniform strain model only defines the composite bulk modulus as a convex combination of the species bulk moduli in regions where all of the Grüneisen exponents are positive. We can expect difficulties with this model for materials that can assume negative Grüneisen in the flow of interest.

Examining equation (80) we see that a compressive wave ($\frac{DP}{Dt} > 0$) repartitions entropy by taking heat from species with bulk moduli greater than the composite bulk modulus and assigning it to species with bulk moduli less than the composite value. Since this model should only be

used for mixtures with positive Grüneisen exponents, this means that compressive waves cause more compressible (small bulk modulus) materials to relatively gain heat and less compressible materials to relatively cool. Similarly we see from (81) that for thermally isolated mixtures the less compressible materials gain relative volume at the expense of the more compressible species. Of course, neither extreme can be completely correct since the differential response of the separate materials to compression waves should result in an interaction between materials that exchanges both heat (via P-V work between materials) and volume (via differential compression). Indeed a physical basis for the selection of the modeling parameters δ_k could be based on an attempt to approximate these interactions. It is also interesting to note that if we wish to preserve the conditions that compressible materials relatively gain heat and lose volume in a compression wave, then this implies that the model coefficients satisfy $-1 \leq \delta_k \leq 1$.

Pressure-Temperature Equilibrium

Since pressure-temperature equilibrium implies a single mixture sound speed, this model satisfies equation (51) and so should be of the form (60)–(65). To establish this explicitly, we first note that thermodynamics relates changes in pressure, temperature, and entropy for a pure material:

$$T\mathrm{d}S = -T\beta V\mathrm{d}P + C_P\mathrm{d}T. \tag{82}$$

Here β is the coefficient of thermal expansion and C_P is the specific heat at constant pressure. Next, using the P-T equilibrium entropy equation

$$\sum_{k=1}^{N} \mu_k T \frac{DS_k}{Dt} = 0, \tag{83}$$

we obtain:

$$T\sum_{k=1}^{N} \mu_k V_k \beta_k \frac{DP}{Dt} = T\sum_{k=1}^{N} \alpha_k \beta_k V \frac{DP}{Dt} = T\beta V \frac{DP}{Dt} = \sum_{k=1}^{N} \mu_k C_{P,k} \frac{DT}{Dt} = C_P \frac{DT}{Dt}. \tag{84}$$

Where β is the volume fraction weighted sum of the species β_k, the mixture specific heat at constant pressure is the mass fraction weighted sum the species specific heats, and the total specific volume V is the mass fraction weighted sum of the species specific volumes. Equations (82) and (84) then imply that for pressure-temperature equilibrium flows, the separate species specific entropies and volume fractions evolve as:

$$T\frac{DS_k}{Dt} = C_{P,k}T\left[\frac{\beta V}{C_P} - \frac{\beta_k V_k}{C_{P,k}}\right] \frac{DP}{Dt},$$
$$\frac{D\alpha_k}{Dt} = \alpha_k \left\{(\beta_k - \beta)\Gamma T + \rho c^2 (K_T - K_{T,k})\right\} \frac{1}{\rho c^2} \frac{DP}{Dt}. \tag{85}$$

Comparing (85) with (53) we obtain:

$$\frac{1+\delta_k}{2} = \frac{(K_T - K_{T,k}) + \frac{\Gamma T}{\rho c^2}(\beta_k - \beta)}{\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2}} = (1+\Gamma\beta T) \frac{(K_T - K_{T,k}) + \frac{\Gamma T}{\rho c^2}(\beta_k - \beta)}{(K_T - K_{T,k}) + \frac{T}{\rho_k c_k^2}(\Gamma_k \beta_k - \Gamma\beta)}. \tag{86}$$

A model of the form (53) can be obtained by rewriting (86) as:

$$\frac{1+\delta_k}{2} = (1+\Gamma_{eq}\beta_{eq}T_{eq}) \frac{(K_{T,eq} - K_{T,k}) + \frac{\Gamma_{eq}V}{c_{eq}^2}(\beta_k T_k - \beta_{eq}T_{eq})}{(K_{T,eq} - K_{T,k}) + \frac{V_k}{c_k^2}(\Gamma_k \beta_k T_k - \Gamma_{eq}\beta_{eq}T_{eq})}. \tag{87}$$

6   Shock Structure

The issue of shocks for the system (60)–(65) is problematic since it is not in conservation form. It is easy to show that for bounded source terms, the conservation of species mass, total momentum and total energy yield the Hugoniot equations:

$$s\left[\rho\right] = \left[\rho\mathbf{u}\bullet\mathbf{n}\right], \qquad s\left[\mu_k\rho\right] = \left[\mu_k\rho\mathbf{u}\bullet\mathbf{n}\right],$$
$$s\left[\rho\mathbf{u}\right] = \left[\rho\mathbf{u}\bullet\mathbf{nu} + P\mathbf{n}\right], \tag{88}$$
$$s\left[\rho\left(e + \frac{1}{2}u^2\right)\right] = \left[\mathbf{u}\bullet\mathbf{n}\left(\rho\left(e + \frac{1}{2}u^2\right) + P\right)\right].$$

Here $\mathbf{n}$ is the unit normal to the wave front, and s is the front velocity in the normal direction, and the superscripts 0 and 1 denote the flow state ahead and behind the wave, respectively. From (88) we then derive:

$$\rho^0\left(\mathbf{u}^0\bullet\mathbf{n} - s\right) = \rho^1\left(\mathbf{u}^1\bullet\mathbf{n} - s\right) = -m,$$
$$\left[\mu_k\right]m = 0,$$
$$m\left[\mathbf{u}\right]\bullet\mathbf{n} = \left[P\right], \quad m\left[\mathbf{u} - \left(\mathbf{u}\bullet\mathbf{n}\right)\mathbf{n}\right] = 0, \tag{89}$$
$$m\left\{\left[e\right] + \bar{P}\left[V\right]\right\} = 0.$$

The quantity m is the mass flux across the wave. If the mass flux is non-zero, we obtain the usual shock Hugoniot equation:

$$e^1 - e^0 = \frac{P^1 + P^0}{2}\left(V^0 - V^1\right),$$
$$\mu_k^1 = \mu_k^0,$$
$$\left[\mathbf{u}\right] + m\left[V\right]\mathbf{n} = 0, \quad m\left[\mathbf{u}\right] = \left[P\right]\mathbf{n}, \tag{90}$$
$$s = \mathbf{u}^0\bullet\mathbf{n} + V^0 m = \mathbf{u}^1\bullet\mathbf{n} + V^1 m.$$

Equations (90) imply $m^2 = \frac{P^1 - P^0}{V^0 - V^1}$.

Since the total specific internal energy and specific volume satisfy $e = \sum\limits_{k=1}^{N}\mu_k e_k$ and $V = \sum\limits_{k=1}^{N}\mu_k V_k$, the continuity of mass fractions across a shock gives us the Hugoniot equation for the mixture:

$$\sum_{k=1}^{N}\mu_k\left[e_k\left(P, S_k\right) - e_k^0 - \frac{P + P^0}{2}\left(V_k^0 - V_k(P, S_k)\right)\right] = 0. \tag{91}$$

For simplicity of notation we have dropped the superscript for the quantities behind the shock, which in the following will also correspond to the non-superscripted quantities. Equation (91) is under-determined for more than one material and thus does not uniquely define the thermodynamic state behind the shock. Since the mass fractions are constant across a shock, we have $N - 1$ degrees of freedom to determine the specific entropies (or equivalent) behind a shock given the behind shock pressure. For models of the form (51) solutions to (91) should be further constrained to satisfy the Lax stability criteria:

$$\mathbf{u}^0\bullet\mathbf{n} + c^0 < s < \mathbf{u}\bullet\mathbf{n} + c, \quad 0 < m,$$
$$\mathbf{u}\bullet\mathbf{n} - c < s < \mathbf{u}^0\bullet\mathbf{n} - c^0, \quad m < 0. \tag{92}$$

Using the formula for the shock speed from equation (90) we see that the Lax stability condition is equivalent to the inequality:

$$\rho^0 c^0 < |m| < \rho c. \tag{93}$$

In particular inequality (93) implies that the mass flux across the shock should converge to the acoustic impedance ρc as the shock strength goes to zero.

We note that system (91) is a convex combination of individual species Hugoniot equations, and an obvious solution is given by choosing the separate specific entropies to satisfy the single species Hugoniot equations. However this cannot be the case in general, for example for P-T equilibrium mix the flow behind the shock is further constrained to be in temperature equilibrium which would be inconsistent with the separate Hugoniot temperatures.

However the separate Hugoniot solution for (91) does seem reasonable for the thermal isolation model. For this model the mixture sound speed is:

$$\frac{1}{\rho^2 c^2} = \sum_{k=1}^{N} \frac{\mu_k}{\rho_k^2 c_k^2}. \tag{94}$$

While the separate Hugoniot mass flux satisfies:

$$\frac{1}{m^2} = \frac{V^0 - V}{P - P^0} = \sum_{k=1}^{N} \mu_k \frac{V_k^0 - V_{H,k}\left(P, P^0, V_k^0\right)}{P - P^0} = \sum_{k=1}^{N} \frac{\mu_k}{m_{H,k}^2\left(P, P^0, V_k^0\right)}. \tag{95}$$

In Menikoff and Plohr [18], section IV.A it is shown that for materials with positive fundamental derivative of gas dynamics [35, 36]:

$$\mathcal{G} \equiv \frac{1}{2} \frac{V^2}{\rho c^2} \left.\frac{\partial^2 P}{\partial V^2}\right|_S. \tag{96}$$

The Hugoniot mass flux satisfies for $P^0 < P$:

$$\rho_k^0 c_k^0 < |m_k| < \rho_k c_k,$$
$$\frac{1}{\left(\rho_k c_k\right)^2} < \frac{1}{m_k^2} < \frac{1}{\left(\rho_k^0 c_k^0\right)^2}. \tag{97}$$

Taking the mass average of the second of inequality (97) implies the Lax condition:

$$\rho^0 c^0 < |m| < \rho c. \tag{98}$$

In addition, Menikoff and Plohr (section IV.B) also show that for positive $\mathcal{G}$, the specific entropy increases with the pressure behind the shock and hence the mass averaged entropy increases across a shock for such mixtures. In view of the above discussion and since most common materials have a positive fundamental derivative of gas dynamics for almost their entire equation of state domain; we will restrict our attention to mixtures of components all of which satisfy $\mathcal{G}_k > 0$ for the thermodynamic flow domain being considered.

A problem with the separate Hugoniot solution is that each material has a different shock velocity and hence velocity equilibrium may not be satisfied behind the shock. The separate Hugoniot model for thermal isolation is essentially the statement that the interaction between the waves produced by refractions and reflections through the subgrid interfaces equilibrates

the velocity to the value given by equation (90) without substantially changing the pressure behind the shock.

The general case for models of the form (53) is even more problematic. For example, the natural assumption for the uniform strain Hugoniot would be to enforce the condition $[\alpha_k] = 0$ across shocks. Indeed this condition must be asymptotically satisfied for weak shocks in order to preserve the continuity of the shock locus with the rarefaction locus at zero strength shocks. With this assumption we see that the micro-specific volume jump condition becomes:

$$\alpha_k \, [V] = \mu_k \, [V_k] \,, \tag{99}$$

and our Hugoniot condition is:

$$\sum_{k=1}^{N} \mu_k e_k \left(P, V_k^0 + \tfrac{\alpha_k}{\mu_k}(V - V^0 t) \right) - e^0 = \frac{P + P^0}{2}(V^0 - V). \tag{100}$$

If for fixed α_k, μ_k and V_k^0 we define an internal energy:

$$\bar{e}(P, V) = \sum_{k=1}^{N} \mu_k e_k \left(P, V_k^0 + \tfrac{\alpha_k}{\mu_k}(V - V^0) \right), \tag{101}$$

we see that equation (100) is simply the Hugoniot equation for the equation of state defined by (101) with ahead state $\left(P^0, V^0 \right)$. It is a straightforward exercise to show that the sound speed for the equation of state given by (101) is the same as the uniform strain sound speed at the given mass and volume fractions:

$$\frac{\rho c^2}{\Gamma} = \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k} \rho_k c_k^2, \quad \frac{1}{\Gamma} = \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k}. \tag{102}$$

Here Γ is the Grüneisen exponent for EOS (101). As previously stated, the mixture sound speed formula suggests that the uniform strain mixture model is most reasonable for positive Grüneisen exponents, which we assume in the following. The definition of the adiabatic exponent $\gamma = \frac{c^2}{PV}$ shows that the Grüneisen and adiabatic exponents for EOS (101) are related to the component values by the equations:

$$\frac{\gamma}{\Gamma} = \sum_{k=1}^{N} \alpha_k \frac{\gamma_k}{\Gamma_k}, \quad \frac{1}{\Gamma} = \sum_{k=1}^{N} \alpha_k \frac{1}{\Gamma_k}. \tag{103}$$

A straightforward application of equation (40) in Menikoff and Plohr [18] shows that the fundamental derivative of gas dynamics can be written:

$$\mathcal{G} = \frac{\Gamma}{2} \left\{ \frac{\gamma + 1}{\Gamma} + \left(P \left. \frac{\partial \gamma / \Gamma}{\partial P} \right|_V - \frac{V}{\gamma} \left. \frac{\partial \gamma / \Gamma}{\partial V} \right|_P \right) - \gamma \left(P \left. \frac{\partial 1/\Gamma}{\partial P} \right|_V - \frac{V}{\gamma} \left. \frac{\partial 1/\Gamma}{\partial V} \right|_P \right) \right\}. \tag{104}$$

Using equation (104) we then find that the fundamental derivative of gas dynamics for EOS (101) is given by:

$$\mathcal{G} = \Gamma \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k} \mathcal{G}_k + \frac{\Gamma}{2} \sum_{k=1}^{N} \alpha_k \left(\gamma - \gamma_k \right) \left[\frac{V_k}{\gamma \gamma_k} \left. \frac{\partial \gamma_k / \Gamma_k}{\partial V_k} \right|_P - P \left. \frac{\partial 1/\Gamma_k}{\partial P} \right|_{V_k} \right]. \tag{105}$$

Two easy cases are now obvious, for perfect gases $\gamma > 0$ and $\Gamma = \gamma - 1$ are constant, while for stiffened gamma law gases [15] $\Gamma > 1$ is constant while $\gamma = (\Gamma + 1)\frac{P+P_\infty}{P}$ is independent of specific volume (P_∞ being an EOS parameter). Thus in both cases we get that the mixture fundamental derivative is positive and in fact is equal to $\frac{\Gamma}{2}$.

However for the general case, it is not obvious at all that positivity of the component fundamental derivatives imply positivity of the mixture fundamental derivative, raising the possibility that such mixtures could exhibit non-convex type behaviors such as shock splitting as described in the Menikoff and Plohr [18] paper (see section V).

7   Application: Radiation Hydrodynamics

We consider a radiation hydrodynamic flow with pressure and velocity equilibrium between material components. For simplicity we assume non-reactive components and a single radiation energy the interacts with all of the material components and furthermore we assume that the radiation flow can be modeled in the diffusion limit [19, 40]. The conservation of mass, momentum, and energy laws then become:

$$
\begin{aligned}
&\frac{\partial \alpha_k \rho_k}{\partial t} + \nabla \cdot (\alpha_k \rho_k) = 0, \\
&\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla (P + P_r) = \rho \mathbf{g}, \\
&\frac{\partial \left[\rho\left(\frac{1}{2}u^2 + e\right) + E_r\right]}{\partial t} + \nabla \cdot \left[\rho \mathbf{u}\left(\frac{1}{2}u^2 + e\right) + E_r \mathbf{u} + (P + P_r)\mathbf{u} + \mathbf{F}_r\right] = \rho \mathbf{u} \cdot \mathbf{g}.
\end{aligned}
\tag{106}
$$

Here E_r is the radiation energy density (units: energy/volume), P_r is the radiation pressure, and $\mathbf{F}_r$ is the radiation flux. Expanding the energy conservation component (line three of equation (106)) and using the mass and momentum conservation laws we can derive:

$$
\begin{aligned}
&\rho\left[\frac{De}{Dt} + P\frac{DV}{Dt}\right] + \frac{\partial E_r}{\partial t} + \nabla \cdot [E_r \mathbf{u} + \mathbf{F}_r] + P_r \nabla \cdot \mathbf{u} = 0, \\
&\frac{\partial E_r}{\partial t} + \nabla \cdot [E_r \mathbf{u} + \mathbf{F}_r] + P_r \nabla \cdot \mathbf{u} = -\rho\left[\frac{De}{Dt} + P\frac{DV}{Dt}\right] = -\rho q.
\end{aligned}
\tag{107}
$$

We can then rewrite equation (106) is a form similar to that of equation (41) by defining $\mathbf{b} = \mathbf{g} - \frac{\nabla P_r}{\rho}$ and $\frac{\partial E_r}{\partial t} + \nabla \cdot [E_r \mathbf{u} + \mathbf{F}_r] + P_r \nabla \cdot \mathbf{u} = -\rho q$.

System (106) is closed by specifying evolution equations for the specific entropy or volume fractions of each component as in equation (53).

$$
\begin{aligned}
&T_k \frac{DS_k}{Dt} = -\frac{c_k^2}{\Gamma_k}\left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2}\right]\left(\frac{1-\delta_k}{2}\right)\frac{DP}{Dt} + q_k \iff \\
&\frac{D\alpha_k}{Dt} = \alpha_k\left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2}\right]\left(\frac{1+\delta_k}{2}\right)\frac{DP}{Dt} + \alpha_k\left(\frac{\Gamma_k}{c_k^2}q_k - \mathcal{S}\right), \\
&\frac{DP}{Dt} + \rho c^2 \nabla \cdot \mathbf{u} = \rho c^2 \mathcal{S}, \quad \mathcal{S} = \sum_{k=1}^{N} \alpha_k \frac{\Gamma_k q_k}{c_k^2},
\end{aligned}
$$

$$\rho c^2 \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k} \left(\frac{1-\delta_k}{2}\right) = \sum_{k=1}^{N} \frac{\alpha_k}{\Gamma_k} \left(\frac{1-\delta_k}{2}\right) \rho_k c_k^2 \iff$$

$$\frac{1}{\rho c^2} \sum_{k=1}^{N} \alpha_k \left(\frac{1+\delta_k}{2}\right) = \sum_{k=1}^{N} \alpha_k \left(\frac{1+\delta_k}{2}\right) \frac{1}{\rho_k c_k^2}. \tag{108}$$

Using the evolution equation for material pressure in (66) to substitute for the total derivative of pressure in the first two equations, we can rewrite this system as:

$$T_k \frac{DS_k}{Dt} = \frac{c_k^2}{\Gamma_k} \left[1 - \frac{\rho c^2}{\rho_k c_k^2}\right] \left(\frac{1-\delta_k}{2}\right) \nabla \cdot \mathbf{u} - \frac{c_k^2}{\Gamma_k} \left[1 - \frac{\rho c^2}{\rho_k c_k^2}\right] \left(\frac{1-\delta_k}{2}\right) \mathcal{S} + q_k,$$

$$\frac{D\alpha_k}{Dt} = -\alpha_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2}\right] \left(\frac{1+\delta_k}{2}\right) \nabla \cdot \mathbf{u} + \alpha_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2}\right] \left(\frac{1+\delta_k}{2}\right) \mathcal{S} + \alpha_k \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S}\right), \tag{109}$$

$$P = P\left(e, V, \vec{\alpha}, \vec{\mu}\right), e_k = e_k(e, V, \vec{\alpha}, \vec{\mu}), \mu_k V_k = \alpha_k V, T_k = T_k\left(e_k, V_k\right).$$

Here the constitutive relations for the pressure, component specific internal energies, and temperatures are given by the solution to system (68)–(70) together with the component equation of state.

The closure formulas in equation (109) together with the relations $de_k + PdV_k = T_k dS_k$, $e = \sum_{k=1}^{N} \mu_k e_k$, $V = \sum_{k=1}^{N} \mu_k V_k$, and $\frac{D\mu_k}{Dt} = 0$ allow us to rewrite equation (107) as:

$$\frac{\partial E_r}{\partial t} + \nabla \cdot \left[E_r \mathbf{u} + \mathbf{F}_r\right] + P_r \nabla \cdot \mathbf{u} = -\rho q,$$

$$\frac{\partial \left[\rho \left(\frac{1}{2}u^2 + e\right)\right]}{\partial t} + \nabla \cdot \left[\rho \mathbf{u}\left(\frac{1}{2}u^2 + e\right) + P\mathbf{u}\right] + \mathbf{u} \cdot \nabla P_r = \rho \mathbf{u} \cdot \mathbf{g} + \rho q. \tag{110}$$

This version will be useful in the operator split discussion below.

Our primary interest will be for the thermal isolation ($\delta_k = 1$) or uniform strain ($\delta_k = -1$) cases, although this class of models also includes temperature equilibrium (equation (87)) as a special case.

Up to now, this discussion is purely formal; it remains to specify the form of the heat source terms q_k. We assume a very simply phenomenological model for the interaction of the radiation field with the material components, namely that the radiation field interacts with each material component separately via a non-equilibrium relaxation between the material temperature field and the radiation field:

$$q_k = -V_k c_L \kappa_k \left(V_k, T_k\right) \left(a_R T_k^4 - E_r\right). \tag{111}$$

Here c_L is the speed of light, $a_R = 7.56 \times 10^{-15}$ erg/cm^3/ deg^4 is the radiation constant, and $\kappa_k \left(V_k, T_k\right)$ is the absorption mean opacity, which we regard as a constitutive function of the component specific volume and temperature. For this simple model, we take $P_r = \frac{1}{3}E_r$ and a gray diffusion radiation flux $\mathbf{F}_r = -\frac{c_L}{3\bar{\chi}} \nabla E_r$ where $\bar{\chi} = \sum_{k=1}^{N} \alpha_k \bar{\chi}_k \left(V_k, T_k\right)$ is the total mean opacity which is computed as the volume average of the component mean opacities regarded as constitutive functions of the component specific volume and temperature. This model is a straightforward generalization to multiple component temperatures of the gray diffusion material equilibrium model described in Mihalas&Mihalas [19] (§97, equations 97.70-97.94), and as such may be subject to various physical limitations not discussed further here.

With these closures, system (106)/(111) might be solved using operator splitting between the hydrodynamic component and the radiation component. Specifically, the hydrodynamic component becomes:

$$
\begin{aligned}
&\frac{\partial \alpha_k \rho_k}{\partial t} + \nabla \cdot (\alpha_k \rho_k) = 0, \\
&\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla P = \rho \mathbf{g}, \\
&\frac{\partial \left[\rho \left(\frac{1}{2} u^2 + e \right) \right]}{\partial t} + \nabla \cdot \left[\rho \mathbf{u} \left(\frac{1}{2} u^2 + e \right) + P \mathbf{u} \right] = \rho \mathbf{u} \cdot \mathbf{g}, \\
&\frac{\partial E_r}{\partial t} + \nabla \cdot (\mathbf{u} E_r t) = 0, \\
&\frac{D \alpha_k}{Dt} = \alpha_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{1 + \delta_k}{2} \right) \nabla \cdot \mathbf{u}, \\
&P = P\left(e, V, \vec{\alpha}, \vec{\mu} \right), e_k = e_k\left(e, V, \vec{\alpha}, \vec{\mu} \right), \mu_k V_k = \alpha_k V, T_k = T_k\left(e_k, V_k \right).
\end{aligned}
\tag{112}
$$

While the radiation component is:

$$
\begin{aligned}
&\frac{\partial \alpha_k \rho_k}{\partial t} = 0, \\
&\frac{\partial \rho u}{\partial t} + \nabla P_r = 0, \\
&\frac{\partial \left[\rho \left(\frac{1}{2} u^2 + e \right) \right]}{\partial t} + \mathbf{u} \cdot \nabla P_r = \rho q, \\
&\frac{\partial E_r}{\partial t} + \nabla \cdot \mathbf{F}_r + P_r \nabla \cdot \mathbf{u} = -\rho q, \\
&\frac{\partial \alpha_k}{\partial t} = \alpha_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{1 + \delta_k}{2} \right) \mathcal{S} + \alpha_k \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S} \right), \\
&P = P(e, V, \vec{\alpha}, \vec{\mu}), e_k = e_k\left(e, V, \vec{\alpha}, \vec{\mu} \right), \mu_k V_k = \alpha_k V, T_k = T_k\left(e_k, V_k \right)?
\end{aligned}
\tag{113}
$$

With the source term q given by:

$$
\begin{aligned}
q &= \sum_{k=1}^{N} \mu_k q_k = - \sum_{k=1}^{N} \mu_k V_k c_L \kappa_k \left(V_k, T_k \right) \left(a_R T_k^4 - E_r \right) \\
&= -V \sum_{k=1}^{N} \alpha_k V_k c_L \kappa_k \left(V_k, T_k \right) \left(a_R T_k^4 - E_r \right) = -V c_L \kappa \left(a_R \tilde{T}^4 - E_r \right), \\
\kappa &= \sum_{k=1}^{N} \alpha_k \kappa_k \left(V_k, T_k \right), \quad \kappa \tilde{T}^4 = \sum_{k=1}^{N} \alpha_k \kappa_k \left(V_k, T_k \right) T_k^4.
\end{aligned}
\tag{114}
$$

Since $\rho = \sum_{k=1}^{N} \alpha_k \rho_k$, we immediately see that, for the radiation operator split component, density is constant in time. Also, since $\alpha_k \rho_k = \mu_k \rho$ we see that the mass fractions are also constant in time for the radiation step. Using these two observations together with the momentum equation in (113) allows us to rewrite the radiation energy update equation as:

$$
\frac{\partial \alpha_k \rho_k}{\partial t} = 0,
$$

$$\rho \frac{\partial u}{\partial t} + \nabla P_r = 0,$$

$$\rho \frac{\partial e}{\partial t} = \rho q,$$

$$\frac{\partial E_r}{\partial t} + \nabla \cdot \mathbf{F}_r + P_r \nabla \cdot \mathbf{u} = -\rho q, \tag{115}$$

$$\frac{\partial \alpha_k}{\partial t} = \alpha_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{1 + \delta_k}{2} \right) \mathcal{S} + \alpha_k \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S} \right),$$

$$P = P(e, V, \vec{\alpha}, \vec{\mu}), e_k = e_k(e, V, \vec{\alpha}, \vec{\mu}), \mu_k V_k = \alpha_k V, T_k = T_k(e_k, V_k)?$$

System (115) is then further split into hyperbolic and parabolic components.

Hyperbolic component

$$\rho \frac{\partial u}{\partial t} + \nabla P_r = 0,$$

$$\frac{\partial E_r}{\partial t} + P_r \nabla \cdot \mathbf{u} = 0, \tag{116}$$

$$\frac{\partial \rho}{\partial t} = 0.$$

Since density is constant in time for system (116), and $P_r = \frac{1}{3} E_r$, this system equivalent to a 2×2 hyperbolic system with characteristics $\lambda = \pm \frac{1}{3} \sqrt{\frac{E_r}{\rho}}$.

Parabolic component

$$\frac{\partial V}{\partial t} = 0, \quad \frac{\partial \mu_k}{\partial t} = 0,$$

$$\frac{\partial e}{\partial t} = q,$$

$$\frac{\partial E_r}{\partial t} + \nabla \cdot \mathbf{F}_r = -\rho q, \tag{117}$$

$$\frac{\partial \alpha_k}{\partial t} = \alpha_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{1 + \delta_k}{2} \right) \mathcal{S} + \alpha_k \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S} \right).$$

This system is closed by the pressure equilibrium assumption (68)–(70) that gives all of the thermodynamic quantities (e.g. sound speeds and Grüneisen exponents) as functions for the total specific volume, total specific internal energy, the mass fractions, and the volume fractions. In addition the source terms q and $\mathcal{S}$ are also functions of the radiation energy via the formulas (111) and the definition of $\mathcal{S}$ in equation (108).

One can write direct evolution equations for the component specific volumes, specific entropies, and temperatures in (117). Using the equation for volume fraction update in (117) together with the constitutive relations for the equation of state derivatives in equation (77) we can derive:

$$\frac{\partial P}{\partial t} = \rho c^2 \mathcal{S},$$

$$\frac{\partial V_k}{\partial t} = V_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{1 + \delta_k}{2} \right) \mathcal{S} + V_k \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S} \right),$$

$$T_k \frac{\partial S_k}{\partial t} = -\frac{c_k^2}{\Gamma_k} \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{1 - \delta_k}{2} \right) \mathcal{S} + q_k,$$

$$\frac{\partial e_k}{\partial t} = T_k \frac{\partial S_k}{\partial t} - P \frac{\partial V_k}{\partial t},$$

$$\frac{\partial T_k}{\partial t} = -\frac{\Gamma_k T_k}{V_k} \frac{\partial V_k}{\partial t} + \frac{1}{C_{V,k}} T_k \frac{\partial S_k}{\partial t},$$

$$\frac{\partial e_k}{\partial t} = C_{V,k} \frac{\partial T_k}{\partial t} + \left[C_{V,k} T_k - \frac{P V_k}{\Gamma_k} \right] \frac{\Gamma_k}{V_k} \frac{\partial V_k}{\partial t}.$$

If we differentiate the expression for $\tilde{T}$ in equation (114) we obtain:

$$4\kappa \tilde{T}^3 \mathrm{d}\tilde{T} = \sum_{k=1}^{N} \alpha_k \kappa_k \left\{ \left[4T_k^4 + (T_k^4 - \tilde{T}^4) \frac{\partial \log \kappa_k}{\partial \log T_k} \right] \frac{\mathrm{d}T_k}{T_k} \right.$$
$$\left. + (T_k^4 - \tilde{T}^4) \left[\frac{\mathrm{d}\mu_k}{\mu_k} + \left[1 + \frac{\partial \log \kappa_k}{\partial \log V_k} \right] \frac{\mathrm{d}V_k}{V_k} \right] \right\}. \tag{118}$$

This expression when used in combination with equations (118) can be used to derive an explicit time update formula for the opacity averaged temperature:

$$\frac{1}{\tilde{T}} \frac{\partial \tilde{T}}{\partial t} = \sum_{k=1}^{N} \frac{\alpha_k \kappa_k}{\kappa} \left\{ \frac{T_k^4}{\tilde{T}^4} \left(\frac{q_k}{C_{V,k} T_k} - \Gamma_k \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S} \right) - \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{c_k^2}{\Gamma_k C_{V,k} T_k} \left(\frac{1 - \delta_k}{2} \right) \right. \right. \right.$$
$$\left. + \Gamma_k \left(\frac{1 + \delta_k}{2} \right) \right) \mathcal{S} + \frac{(T_k^4 - \tilde{T}^4)}{4\tilde{T}^4} \left(\frac{\partial \log V_k \kappa_k}{\partial \log S_k} \bigg|_{V_k} \frac{q_k}{S_k T_k} \right.$$
$$+ \frac{\partial \log V_k \kappa_k}{\partial \log V_k} \bigg|_{S_k} \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S} \right) + \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{\partial \log V_k \kappa_k}{\partial \log V_k} \bigg|_{S_k} \left(\frac{1 + \delta_k}{2} \right) \right.$$
$$\left. \left. \left. - \frac{\partial \log V_k \kappa_k}{\partial \log S_k} \bigg|_{V_k} \frac{c_k^2}{\Gamma_k S_k T_k} \left(\frac{1 - \delta_k}{2} \right) \right) \mathcal{S} \right) \right\}. \tag{119}$$

This complicated expression can be useful in assessing the relative contributions of the separate components in the rate of change of the opacity averaged temperature.

Equation (117) is still quite complicated. In order to simplify the solver we propose one more operator split step:

Fixed-Radiation Volume Advection

$$\frac{\partial V}{\partial t} = 0, \quad \frac{\partial \mu_k}{\partial t} = 0, \frac{\partial e}{\partial t} = 0, \frac{\partial E_r}{\partial t} = 0,$$

$$\frac{\partial V_k}{\partial t} = V_k \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \left(\frac{1 + \delta_k}{2} \right) \mathcal{S} + V_k \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S} \right), \tag{120}$$

$$\alpha_k V_k = \mu_k V, e = \sum_{k=1}^{N} \mu_k e_k, P = P_k (e_k, V_k).$$

Fixed-Volume-Fraction Radiation Diffusion

$$\frac{\partial V}{\partial t} = 0, \quad \frac{\partial \mu_k}{\partial t} = 0, \quad \frac{\partial V_k}{\partial t} = 0, \quad \frac{\partial \alpha_k}{\partial t} = 0,$$

$$\frac{\partial e}{\partial t} = q,$$

$$\frac{\partial E_r}{\partial t} + \nabla \cdot \mathbf{F}_r = -\rho q, \tag{121}$$

$$\alpha_k V_k = \mu_k V, e = \sum_{k=1}^{N} \mu_k e_k, P = P_k (e_k, V_k).$$

The solution to system (120) gives updated component thermodynamic quantities as functions of the fixed in time (but spatially variable) radiation energy. The closure conditions in the equation of (121) give the thermodynamic variables as functions of the single total specific internal energy for known specific volumes.

8   Conclusion

The main intent of this research note has been to summarize the basic mathematic consequences of assuming a single pressure/velocity model for compressible flows. We saw that such models can be characterized as a $N - 1$ parameter family of flow models in the number of separate material components, corresponding to consistency conditions for two formulas for the system sound speed. In particular three special cases were described, pressure-temperature equilibrium, thermal isolation and uniform strain. The derivations of the characteristic structure of these models will be useful in the design and implementation of compressible flow solvers for such systems, but specific instances of such implementations are not the focus of this note. It is hoped that the formulas derived here will be helpful in clarifying the connection of such models in applications.

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